

Hydrogen Production by Solar Steam Reforming as a Fuel Decarbonization Route

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Abstract This chapter describes the hydrogen production by solar-powered steam reforming. This process allows some upgrading of the reformed fuel (in terms of heat value and environmental impact) and significant reduction (40–50 %) in CO₂ emission to the atmosphere, with respect to the conventional steam reforming process. Additionally, solar steam reforming is presented as an emission-free process: the only carbon-containing by-product stream is well suited for the application of CCS technologies, and the overall process can also be considered as a “fuel pre-combustion decarbonization route”. Application of pressurized membrane reactors for low-temperature steam reforming improves the overall process efficiency and enhances the recovery of CO₂ thanks to its relatively high partial pressure in the by-product stream. The application of SERP technology for in situ CO₂ separation is discussed too.

Keywords Thermochemical hydrogen production • Solar steam reforming • Fuel decarbonization • Membrane reformer

Acronyms

CCS	Carbon Capture and Storage
CSP	Concentrating Solar Power
FC	Fuel Cell
HCNG	Hydrogen Containing Natural Gas
HTF	Heat Transfer Fluid
ICE	Internal Combustion Engine
IMR	Integrated Membrane Reformer
MS	Molten Salt
MSMR	Multi-Stage Membrane Reformer
NG	Natural Gas

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PSA	Pressure Swing Adsorption
PV	Photovoltaic
RES	Renewable Energy Sources
SERP	CO ₂ Sorption Enhanced Reforming Process
SMR	Steam Methane Reforming
SR	Steam Reforming
WGS	Water–Gas-Shift reaction

1 Introduction

The growing interest toward the exploitation of renewable energy sources (RES) has supported the development and optimization of efficient and cost-effective technologies to capture and convert solar energy. Solar photovoltaic (PV) cells and concentrating solar power (CSP) plants are today widespread and mature technologies for power production at the small (decentralized) and large (centralized) scales.

Research is going ahead to make these energy conversion systems more efficient, cost-effective, and competitive with the more traditional fossil fuel-based economy. Meanwhile, besides electrical power generation, other RES applications can be identified, like water desalination or fuel production and refining. The application of solar-thermal power to drive heat demanding thermochemical conversion is one of the most rationale ways to exploit solar energy, by reducing the carbon footprint of chemical conversion and allowing the chemical storage of solar energy. Particularly, in fuel refinery, it is possible to improve the heat value and the environmental impact (i.e. the overall “quality”) of the primary feedstock by the aid of solar energy: in this case, the final product is often called “solar fuel” because it partially or totally drives solar energy in its chemical energy.

This chapter specifically deals with the possibility to power with solar energy, a thermochemical process like steam reforming for hydrogen (or syngas) production. It is shown that this approach leads to major benefits in the hydrogen production process, including reduction in carbon dioxide emissions. Additionally, this process allows partial or total pre-combustion decarbonization of the primary fuel and eases CO₂ capture when membrane reactor or sorption enhanced technology is applied.

2 Thermochemical Processes Powered by Concentrated Solar Energy

Thermochemical processes are highly heat demanding chemical processes which can be powered by renewable energy sources (RES). Among the several available RES technologies, only CSP plants can provide high-temperature heat (>350 °C)

as alternative to conventional fuels, without combustion and flue gas emissions to the atmosphere (Fig. 1).

In the case here considered, a chemical plant converts some feedstock, such as carbon-containing compounds like hydrocarbons (with the possible aid of water), to some products and by-products. Clearly, the main products will be characterized by an added energetic value than the feedstock, resulting from the aid of solar power; additionally, the product may be higher quality chemicals with respect to their efficacy and environmental impact when used (this is the case, for example, when hydrogen is used in fuel cells).

There are several examples of hydrogen production routes by the use of solar energy, following the general scheme represented in Fig. 1. These processes, summarized in Table 1, include solar steam gasification of carbonaceous (solid) materials like coal or petcoke [1], solar methane cracking [2], dry reforming [3] and steam reforming [4]; solar-powered thermochemical water-splitting cycles have been proposed too [5]. In gasification and reforming processes, CO_2 is by-product. Differently, carbon coke (solid) is produced in place of CO_2 in cracking, and for this reason, solar cracking is considered as an “emission-free” hydrogen production route. However, with respect to steam reforming, in cracking, a lower hydrogen production yield is obtained with respect to the hydrocarbon consumption: for example, in CH_4 steam reforming combined with water–gas–shift (Eq. 1):

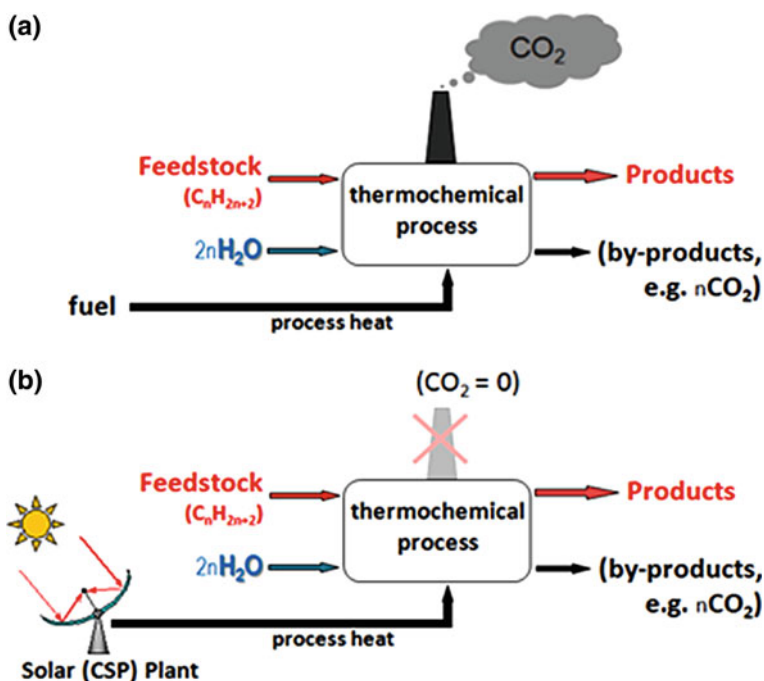
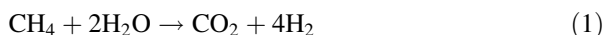


Fig. 1 General concept scheme of a thermochemical process powered by a fuel combustor (a) or by a concentrating solar power (CSP) plant (b) to provide the high-temperature process heat

Table 1 Thermochemical hydrogen production processes possibly driven by solar heat

Process	Feedstock	Main products
Gasification of carbonaceous materials [1]: $C_nH_mO_k + sH_{2(g)} \rightarrow (m/2 + s)H_{2(g)} + (k + s)CO_{(g)} + (n - k - s)C_{(s)}$	Carbon-rich materials (e.g. coke, coal, biomass)	Hydrogen syngas
Hydrocarbon cracking [2]: $C_nH_{2n+2} \rightarrow nC_{(s)} + (n + 1)H_2$	Hydrocarbons (e.g. methane)	Hydrogen carbon black
Dry reforming [3]: $C_nH_{2n+2} + nCO_2 \rightarrow 2nCO_2 + (n + 1)H_2$	Hydrocarbons (e.g. methane)	Hydrogen syngas
Steam reforming [4]: $C_nH_{2n+2} + 2nH_2O \rightarrow nCO_2 + (n + 2)H_2$	Hydrocarbons (e.g. methane)	Hydrogen syngas
Thermochemical water-splitting cycles [5]: $2H_2O \rightarrow 2H_2 + O_2$	Water	Hydrogen oxygen



Half hydrogen moles derive from water, so that a double hydrogen recovery is attained with respect to cracking (Eq. 2):



Finally, thermochemical water-splitting cycles consist of a series of chemical reactions whose overall effect is water decomposition into oxygen and hydrogen, whereas all intermediate chemicals are recycled within the process: if the process heat is provided by a RES like CSP, thermochemical cycles can be considered as a completely carbon-free option for massive hydrogen production alternative to water (alkaline or acidic water) electrolysis. Thermochemical water-splitting cycles are considered an interesting option for the long-term centralized massive hydrogen production, but this is not a mature technology, yet.

On the other hand, steam reforming is the shorter-term option which maximizes the hydrogen output relative to primary fuel consumption, representing today the major hydrogen production route. In this case, hydrogen is produced from hydrocarbons, and CO_2 always figures out as a by-product; when this thermochemical process is powered by renewable heat (e.g. a CSP plant), theoretically there is no combustion in the process and there is just one outlet CO_2 stream, that is, the residual C-containing chemical after hydrogen extraction. Hence, in solar steam reforming, in principle, there are no flue gas emissions from the plant, and the only outlet CO_2 -containing stream is rather concentrated and more easily separated.

Therefore, this approach can be considered as a solar-driven “pre-combustion decarbonization” of fuels, where the carbon cycle of the process has one single output, that is, the process CO_2 by-product stream (Fig. 1).

2.1 Concentrating Solar Plants and Heat Storage

CSP plants consist of mirrors placed on a “solar field”, which track the sun and concentrate the solar radiation several tens or hundred times over a linear tube or spot called “solar receiver” [6]. The solar receiver converts the concentrated solar radiation to heat at temperatures ranging from 350 °C to even more than 1,500 °C, depending on the CSP technology and the “concentration factor” of the solar radiation. Generally, a heat transfer fluid (HTF) is used to remove and transfer the absorbed heat from the receiver to the process by different types of heat exchangers (e.g. steam generators, endothermic chemical reactors, etc.).

There are different available CSP technologies, which differ on the type of receiver, the mirrors shape, tracking system, etc. [6]: solar towers, solar dishes, solar troughs (or linear parabolic collectors), and linear Fresnel collectors. Although these systems have originally been conceived for solar-electrical power production, the same concept can be applied to replace fossil fuels as heat supplier in thermochemical conversion.

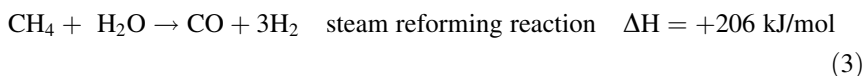
More recent CSP plants make use of molten nitrates as heat transfer fluid and storage medium up to 550–600 °C. Particularly, the molten salt mixture $\text{NaNO}_3/\text{KNO}_3$ (60/40 w/w), often called “solar salt”, has been proposed and positively tested as solar heat carrier and heat storage medium for different types of CSP plants including solar towers, troughs, and linear Fresnel collectors [7–11]. Indeed, the utilization of such storage systems in CSP plants allows mismatch between the renewable heat source and the heat load, ensuring constant-rate solar heat supply also to energy demanding industrial chemical process like the steam reforming [10]. This way, daily start-up and shut-down operations can be avoided regardless the intermittent primary source (i.e. even overnight and during cloudy periods of time).

The application of CSP plants with heat storage by the use of molten nitrates to steam reforming as a fuel decarbonization route is the subject of the following sections.

3 Solar Steam Reforming for Hydrogen Production

In Fig. 2 is represented a simplified block diagram of a typical industrial steam methane reforming (SMR) process. Methane can be derived from natural gas (NG) or other gas sources (e.g. biogas); the case of higher hydrocarbons is similar.

Accordingly, after purification (e.g. sulfur removal) the feed gas is mixed with steam and flowed through a tubular reactor set in an industrial furnace where the steam reforming reaction (Eq. 3) takes place:



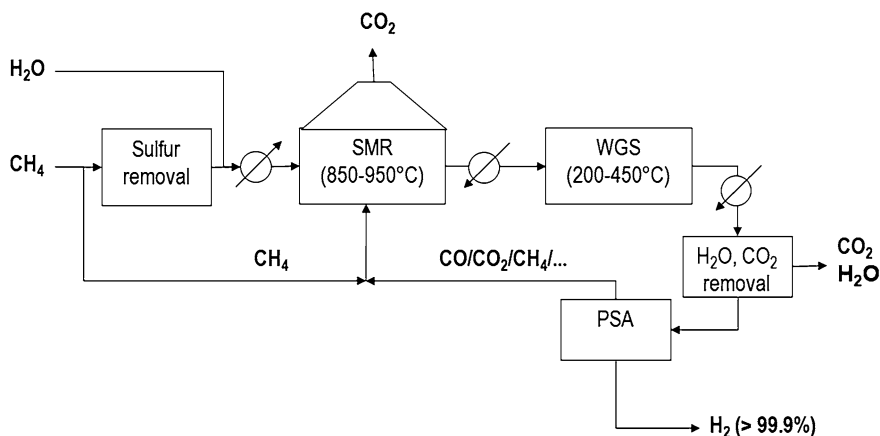


Fig. 2 Simplified block diagram of a typical methane steam reforming process

This reaction is highly endothermic, and satisfactory conversions are usually obtained at high temperatures ($>850\text{ }^{\circ}\text{C}$). For this reason, the combustion of an additional amount of fuel is necessary to sustain the steam reforming reactor.

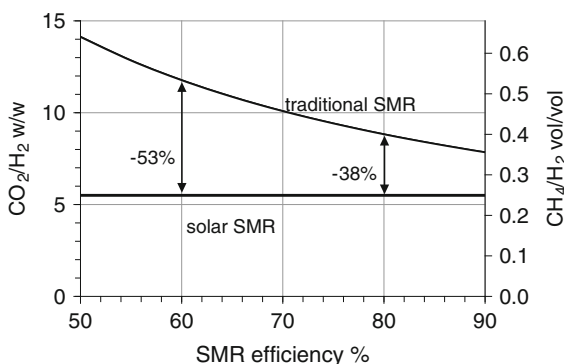
When hydrogen yield has to be maximized, after cooling, the produced syngas is sent to one or more water–gas-shift reactors:



Finally, excess water and CO_2 are removed and the hydrogen purified usually by pressure swing adsorption (PSA).

In general, the high-temperature furnace can be replaced by a CSP plant to (directly or indirectly) drive the process. When the process is powered by solar energy, there is no need of additional fuel to provide the process heat, so that CO_2 containing flue gas emissions to the atmosphere are avoided. Figure 3 shows that solar steam reforming allows a significant fuel save for hydrogen production, with a reduction in CO_2 production/emissions to the atmosphere being the order of

Fig. 3 Comparison of CO_2 emissions and specific methane consumption between the conventional and the renewable-powered SMR routes, as function of overall thermal efficiency (HHV) of the process



40–50 % (outlet CO_2 is $5.5 \text{ kgCO}_2/\text{kgH}_2$, only determined from chemical reactions stoichiometry).

Moreover, carbon balance of the plant evidences a single CO_2 outlet stream with a relatively high CO_2 concentration. This feature enhances the CO_2 recovery by CCS technologies.

When the above-mentioned molten nitrates are used to power the steam reforming reactor, the temperature is limited by the upper temperature of $550\text{--}600^\circ\text{C}$. Therefore, the inner reactor temperature will be within the range of $400\text{--}550^\circ\text{C}$ and the process is referred to as “low-temperature steam reforming” featured by the following major benefits:

- possibility to apply the CSP thermal storage system with molten salts, to mismatch the steady state running chemical process from the fluctuating solar radiation;
- replacement of the high-temperature furnace with a more compact and flameless heat exchanger made of cheaper construction materials (no special alloys for high-temperature operation are required);
- combination of steam reforming and WGS reactions into a single stage at $400\text{--}550^\circ\text{C}$, resulting in a limited CO concentration ($\ll 10 \text{ %vol.}$) in the outlet gas and ca. 20 % reduction in the reformer heat duty.

On the other hand, in low-temperature steam reforming, maximum conversions are thermodynamically limited. Therefore, the downstream hydrogen separation and non-converted feed recovery are major issues which can be resolved using membrane reactors or CO_2 sorption enhanced reforming processes (SERP); otherwise, only a partial conversion of methane should be accepted. All these options are presented in the following sections.

4 Solar Steam Reforming for Fuel Pre-Combustion Decarbonization

In the above sections, it is shown that solar steam reforming is, in principle, an emission-free route for partial or total pre-combustion decarbonization of fuels. This combustion-free process allows fuels conversion into an upgraded fuel like hydrogen, without flue gas emissions, together with enhancement of massive CO_2 recovery by CCS technologies: the introduction of such solar steam reforming plants within the major hydrocarbon transportation lines will allow, besides partial or total fuel decarbonization, the cost-effective CO_2 recovery for subsequent disposal, or re-use by its conversion/allocation in commodities. Thus, a process with zero- CO_2 emissions will be obtained.

This is an interesting opportunity for countries belonging to the so-called “sun belt”, that is, where the exploitation of CSP technology is convenient due to high yearly direct solar radiation (e.g. North Africa or South Europe): solar steam

reforming can be applied for a partial or total pre-combustion decarbonization of NG, with CO_2 recovery in processing stations installed by the major NG pipelines or liquid NG gasification plants.

4.1 Production of Hydrogen/Methane Blends by Steam Reforming with Partial Conversion

A first approach is to accept only a partial methane-to-hydrogen conversion by the low-temperature solar steam reforming route, using the molten salts technology, to obtain hydrogen/methane blends. These gas mixtures are often referred as “hydrogen containing natural gas” (HCNG) that is a useful fuel for different applications in place of pure NG. The process scheme is represented in Fig. 4. Due to thermodynamic limitations after mixing with steam, only partial methane conversion ($<60\%$) can be obtained in a single-pass reactor heated by molten salts at 550°C . Therefore, after excess water condensation, a $\text{CH}_4/\text{H}_2/\text{CO}_2$ stream (SYN), is obtained with a CO_2 content reasonably within the range of $10\text{--}18\%$ vol. Then, CO_2 by-product can be captured (e.g. by regenerative absorption in amine solutions) and compressed for its possible storage (disposal) or re-use. Finally, a

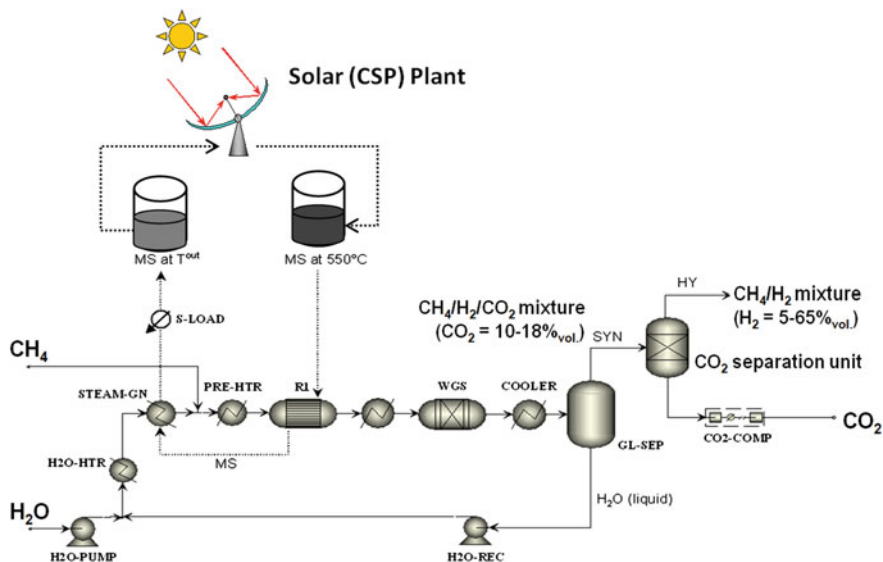


Fig. 4 Basic scheme of a SMR process powered by a CSP plant with molten salt (MS) storage system at 550°C : with a single-pass reactor (R1) for the production of a CH_4/H_2 blend after CO_2 separation

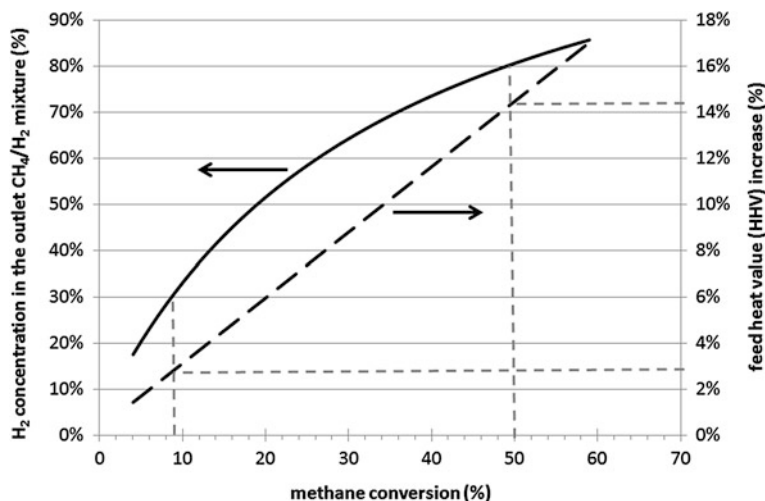


Fig. 5 Relationship between methane conversion (i.e. CH_4 decarbonization rate), composition (%vol. of H_2) of the obtained CH_4/H_2 blend, and the heat value upgrading of the fuel in the low-temperature solar SMR

CH_4/H_2 stream (HY) is obtained with a hydrogen content within the range of 5–65 %vol., depending on the applied working conditions in the reactor (temperature, pressure, space velocity, etc.). Figure 5 reports the relationship between the single-pass methane conversion (i.e. the CH_4 decarbonization rate), the composition of the outlet CH_4/H_2 gas mixture, and the obtained fuel heat value upgrading: for example, 9 % conversion of CH_4 (far below the thermodynamic limit) leads to a HCNG with 30 %vol. of hydrogen and ca. 3 % increase in the fuel heat value; when the CH_4 conversion is increased to 50 %, a HCNG with 80 %vol. of hydrogen and 14.2 % increase in the fuel heat value is obtained.

If applied on a large scale, this simple option for partial NG decarbonization will lead to large hubs with massive CO_2 recovery for subsequent re-use or disposal, without significant modifications to the actual natural gas infrastructure: for injection in the actual NG pipelines, the hydrogen content in HCNG should be limited to ca. 17 %vol. due to pipeline infrastructure limit and different end-use applications [12, 13]. Moreover, some studies demonstrate that actual NG-powered internal combustion engines (ICEs) can accept some hydrogen addition to the fuel, with potential benefits to the engine performance [14]. For instance, this option is studied in the Italian National program METISOL aiming at producing CH_4/H_2 blends up to 30 %vol. using solar energy and the on-board gas storage (in place of pure NG) in light ICE vehicles.

4.2 Production of Pure Hydrogen and Enhanced CO_2 Recovery by Membrane Reformers

Higher methane-to-hydrogen conversions (up to almost total decarbonization) can be obtained by means of devices which “shift” the reaction equilibrium by the removal of (at least) one product. This is the case when hydrogen is extracted using hydrogen-selective membranes usually based on a selective palladium-based layer [10].

In Fig. 6 is represented a general scheme of a membrane reactor involving the three basic transport phenomena of the process: heat transfer through the heat exchanger wall to the catalyst bed, heterogeneous catalysis, and hydrogen permeation through the membrane. Methane conversion increases as the hydrogen product is continuously removed from the reaction mixture (with a flow rate depending on the hydrogen partial pressures on the two sides of the membrane). Thus, high methane conversions (>90 %) can be obtained despite the thermodynamic limitations and two outlet streams will be obtained, as represented in Fig. 7: a pure hydrogen permeate stream (with grade depending on membrane selectivity) and a residual retentate (non-permeate) stream. Due to the high conversions of the hydrocarbon feedstock, the latter stream consists of CO_2 mixed with steam, residual H_2 , and traces of CH_4 and CO . Therefore, after excess water condensation, a by-product stream is obtained with high CO_2 concentration (>50 %vol., depending on the performance of the membrane, i.e. the separation factor). Recovery of CO_2 is also improved by increasing the reformer pressure: although higher pressures are unfavorable to steam reforming thermodynamics, it may be convenient to operate membrane reformers under pressurized conditions (>5 bar) in order to drive the hydrogen permeation through the membrane and minimize the membrane surface.

The relatively high CO_2 concentration and pressure of the by-product stream lead to positive impact in the CO_2 separation: differently from more conventional reforming processes, capture of CO_2 is enhanced by its higher partial pressure which allows application of more cost-effective methods for its recovery and subsequent possible storage (disposal) or re-use.

Indeed, solvents applied to absorb a reasonable amount of CO_2 from dilute low-pressure gases are usually primary and sterically hindered amines. These solvents

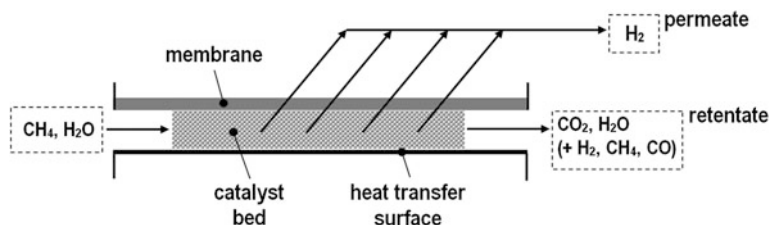


Fig. 6 Membrane reactor scheme for low-temperature steam reforming of methane

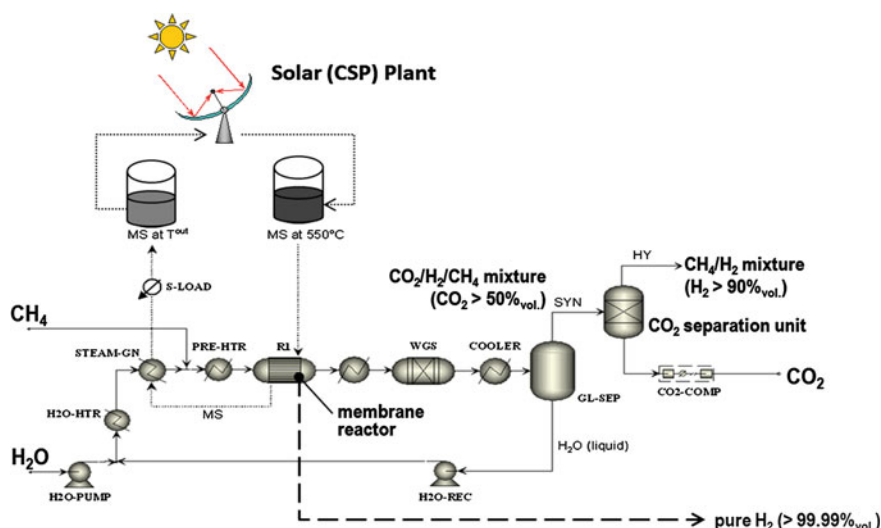


Fig. 7 Basic scheme of a SMR process powered by a CSP plant with molten salt (MS) storage system at 550°C : a membrane reactor (R1) for the production of pure hydrogen and a CO_2 -rich by-product stream

can absorb CO_2 at low pressures because they have high reaction energies. This results in high-energy requirements to regenerate the rich solvent. Differently, when the CO_2 partial pressure is higher (e.g. like the by-product stream from a membrane reformer) costless CO_2 separation methods (in terms of investment and energy duty) can be applied, based on physical principles like physical absorption/stripping [15]. This will result in a significant save ($>50\%$) in the CO_2 capture costs which become competitive, especially when “carbon taxes” are applied.

Besides the production of pure hydrogen (e.g. for FC application) and enhancement of CO_2 recovery, the use of membrane reactors will allow a substantial ($>50\%$) reduction in the process heat duty, with consequent reduction in the overall plant size and cost [10]: in a single-stage process (Fig. 4), a large amount of steam should be generated to produce the hydrogen corresponding to thermodynamic equilibrium; differently, and in membrane reactors (Fig. 7), the same amount of steam leads to larger hydrogen production rates resulting from the higher methane conversion [10].

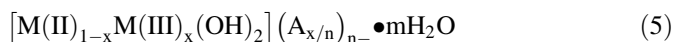
An innovative solar steam reformer powered with molten nitrates is being developed in the framework of the European project CoMETHy (Compact Multifuel Energy to Hydrogen converter) co-funded by the European Commission under the Fuel Cells and Hydrogen Joint Undertaking program (EC Grant Agreement No. 279075). As for the integration of the catalyst with the membrane, two options can be considered: a multi-stage membrane reformer (MSMR) or an integrated membrane reformer (IMR). In the MSMR assembly, the membrane is external to the reactor and a step-by-step increase in methane conversion is obtained thanks to the hydrogen removal in the intermediate membrane units; in

the IMR, the membrane integrated with the catalyst and the heat exchanger. Clearly, the IMR configuration is more compact than the MSMR, but it is more complex, with major engineering and mechanical issues involved in the design.

4.3 Production of Pure Hydrogen by SERP Technology

Besides the membrane exploitation, it is alternatively possible to “shift” the low-temperature steam reforming by the removal of CO₂ product using the so-called sorption enhanced reforming process (SERP). In this case, a solid CO₂ adsorbent is mixed with the steam reforming catalyst for the CO₂ removal as the steam reforming reaction progresses, resulting in the in situ formation of a carbonate; the carbonate can afterward be converted to the respective oxide by either temperature or pressure swing in a regenerative process.

In the perspective of coupling with CSP plants using the “solar salts” technology, specific CO₂ sorbent materials for SERP at 400–550 °C must be applied. Hydrotalcites (also called layered double hydroxides) are promising candidate for this application, consisting of complex Mg and Al oxides, possibly activated with an alkaline carbonate (typically K₂CO₃), with the following general formula:



where M(II) = Mg, M(III) = Al, A = CO₃²⁻, x = 0.25, n = 2.

For example, it is possible to operate the reformer at 350–450 °C and pressures higher than 20 bar and release the CO₂ at 450 °C by pressure swing powered by solar energy, with the co-production of pure CO₂.

The limit of this technology is the relatively low amount of CO₂ adsorbed per unit mass of sorbent material, which is usually lower than 4–5 %wt.

5 Summary and Conclusions

In this chapter, the hydrogen production by solar-powered steam reforming has been presented.

This process basically allows some upgrading of the primary fuel, both in terms of heat value added to the feedstock, and environmental impact at the final user (e.g. when NG is replaced by hydrogen, the energy conversion efficiency is higher with minor pollution).

If compared with the conventional steam reforming processes for hydrogen production, solar-powered steam reforming by itself allows a significant fuel save, with a reduction in the overall CO₂ production and emissions to the atmosphere being the order of 40–50 %.

In fact, in principle, solar steam reforming is an emission-free process because it does not involve combustion and direct CO₂ containing flue gas emissions to the atmosphere. Since the only carbon-containing by-product stream is well suited for the application of CCS technologies, this process can be considered as a “fuel pre-combustion decarbonization route”.

From the point of view of CO₂ recovery, it is shown that this process enhances localized massive production of pure CO₂, pressurized membrane reformers for pre-combustion decarbonization of methane enhanced recovery of pure H₂ and CO₂ as main product and by-product, respectively.

Generally, the application of membranes makes the chemical plant more complex but significantly reduces size and costs of the power plant (heat supplier) by improving overall thermal efficiency of the process. Besides, the use of membrane reactors leads to some positive implication also in CO₂ separation thanks to the relatively high partial pressure of CO₂ in the by-product stream. Finally, the application of SERP technology for in situ CO₂ separation with pure H₂ and CO₂ recovery is considered.

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